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Research note

Application of Multistage Steam Distillation Column for Extraction of Essential Oil of *Valeriana officinialis* L. Cultivated in Iran

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Abstract

Essential oil of Valeriana officinialis L. cultivated in Iran was extracted using steam distillation technique and then analyzed by gas chromatography and gas chromatography-mass spectrometry. Optimization of extraction of essential oil was performed using this technique. The extraction yield results for steam flow rates of 4, 7 and 9 L/min for a packed bed of 100 gram of plant were found to be 0.60, 0.52 and 0.47 percent, respectively. For bed heights of 35, 47.5 and 65 cm and a steam flow rate of 4 L/min the extraction yield was found to be 0.60, 0.36 and 0.24 percent. The results of multistage column for a total of 100 g packed bed and 4 L/min steam flow rate were 0.65, 0.65 and 0.6 for three, two and one stage distillation column, respectively. The oil yield was increased from 0.6 for standard roots to 0.7 for crushing roots.

Keywords: *Multistage Column, Valerian Plant, Essential Oil, Steam Distillation*

1. Introduction

Essential oil of plants has many applications in cosmetic, food and pharmaceutical industries. Valerian officinialis L. is a well-known and frequently used medicinal plant, which has a long proven history of efficacy. The plant is cultivated as a medicinal plant on a commercial scale in the northern parts of Europe and America. Valerian has been shown to encourage sleep, improve sleep quality, and reduce blood pressure [1,2]. The valerian root is sedative, mild anodyne, hypnotic, antispasmodic, carminative, and hypotensive. Traditionally, it has been used for excitability, insomnia, hypochondriasis, migraine, intestinal colic, rheumatic pains, etc. Dried valerian roots alone or with other herbs are also natural repellents of pests, especially cockroaches and skunks [3]. However, it is not fully understood which constituents of *V. officinalis*L., and/or of the other unidentified members of the Valerianaceae family are responsible for the sedative and/or anxiolytic action of valerian extracts.

Valerian essential oil which is present at low concentrations requires exact extraction techniques in order to achieve a high yield.

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Generally, essential oils are produced by different methods: solvent extraction, supercritical fluid extraction, hydrodistillation, steam distillation and supercritical fluid extraction [4-6].

Steam distillation is one of the most popular methods because of its low cost in comparison with technologically advanced methods such as supercritical fluid extraction. Steam distillation has been practiced from the beginning of the 1980s. In the literature there are some studies of oil extraction by steam distillation.

In one study, the effects of the degree of crushing of the plant and time of extraction on the yield and chemical composition of the coriander oil reported that both crushing and distillation time had significant effects on the yield and composition of the oil [7,8].

To the best of our knowledge, only two works have been investigated by the same group on *Valeriana officinalis* L. found in Iran.

Safaralie *et al.* [6] evaluated the composition of essential oil of *Valeriana officinalis* L. roots cultivated in Iran using two techniques, hydrodistillation and CO_2 supercritical extraction (with 15 run) and GC and GC/Mass analytical methods. They have identified forty-seven compounds within Iranian *Valeriana officinalis* L. and interestingly, their results revealed that using CO_2 supercritical extraction technique for extraction of *Valeriana officinalis* L. resulted in higher yields than hydrodistillation and significant difference in essential oil composition. Moreover, some constituents were identified by hydrodistillation although they were not determined by CO_2 supercritical extraction in any experiment. hydrodistillation was also more successful to collect the volatile component than CO_2 supercritical extraction. However, the extraction time for hydrodistillation was reported 2.5 hours whereas CO_2 supercritical extraction was performed in the range of dynamic time from 15 min to 45 min plus 20 min static time [6]. In another work done [5], extraction of essential oil by CO_2 supercritical extraction has been optimized using Experimental design. Under optimum conditions, the yield of essential oil was reported 4.69 to 4.87 w/w [5], however, extraction of essential oil from *Valeriana officinalis* L. found in Iran by other techniques is open for investigation.

This current study will use steam distillation to measure the effects of steam flow rate, height of bed and number of beds on yield of Valerian essential oil cultivated in Iran. In addition, the effect of extraction time on the yield on three of the most important components, camphene, iso-bornyl acetate and valerenal was investigated.

In the present study, a column was designed and constructed in order to evaluate the steam distillation process for the extraction of valerian oil. Optimum operating conditions in order to achieve high extraction yields were determined. Also, we analyzed the effect of distillation time on the chemical composition of extracted valerian oil.

2. Materials and method

2-1. Materials

Valerian plant was collected (December 2006) from Iranian Institute of Medicinal Plants (IMP) research farm and air dried to below 4 % moisture content.

2-2. Steam distillation apparatus and procedure

A schematic diagram of the steam distillation apparatus used for essential oil extraction is shown in Fig. 1.

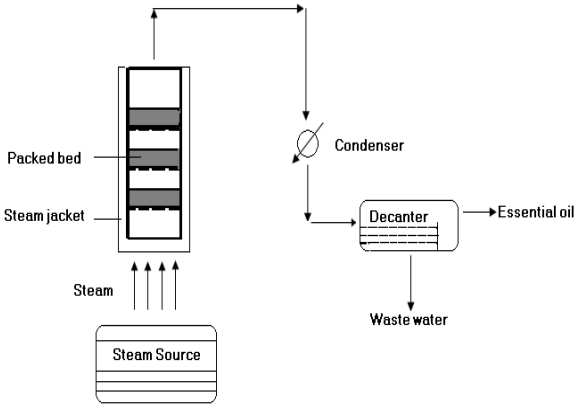

Figure 1. Diagram of the steam distillation extraction process.

The apparatus consists of a reboiler, column insulated with a 1 cm thick foam for steam jacket, condenser and decanter.

The cylindrical Pyrex column has a 6 cm inner diameter and 60 cm hight.

Experiments were performed to study the effect of crushing leaves on the yield of process and distillation time. In these experiments, particle size was 4 mm.

In the first experiment, a batch of 100-200 g of crushed dry leaves of valerian with particle size of 4 mm was packed in the column with 2000 mL water in the reboiler. The column lid was closed and the process of distillation began with the injection of steam from reboiler to the bottom of the column. The plant bed was exposed to several flow rates of steam: 4, 7 and 9 L/min. Steam and essential oils were condensed and collected in time intervals of 45, 90, 135 and 180 minutes. Following condensation, the mixture is decanted in order to separate the oil phase from the water phase. The essential oil is then collected, dried with anhydrous sodium sulphate and stored at 4°C until analyzed. This process is repeated with two and then three plant beds.

The essential oil yield (Y) was estimated according to the ratio of essential oil volume (mL) to dry vegetal matter by using the following equation [1]:

$$Y = \frac{M_{oil}}{M_S} \times 100 \qquad (1)$$

Where:

M_{oil} : Essential oil volume (mL).

M_S : Dry vegetal matter mass (g).

Y : Essential oil yield (mL/100 g dry matter).

After determining the yield with one, two and three beds, samples from the three experiments with steam flow rates of 4, 7 and 9 L/min and a packed bed of 100 g collected in four mentioned time intervals were analyzed by **GC-MS** and **GC** instruments at least three times and a mean value of results was reported.

2-3. Gas chromatography-mass spectrometry identification

GC analyses was carried out using a Hewlett-Packard 6890 with HP-5 capillary column (phenyl methyl siloxane, 25 m×0.25 mm, 0.25 µm film thickness) and a DB-1 capillary column (30 m ×0.25 mm, 0.25 µm film thickness). Other parameters set at GC are as follows:

oven temperature, 60–240°C at 4°C/min; injector temperature, 250°C; detector temperature, 260°C; carrier gas, He (1.5 ml/min); split ratio, 1:25.

GC–MS analyses were carried out by applying a Hewlett-Packard 6859 with a quadropol detector, on a HP-5 column (see GC), operated at 70 eV ionization energy, using the same temperature programmer and carrier gas as mentioned above.

3. Results

Separation of essential oils was performed in single stage and multistage column with three steam flow rates. Fig. 2. represents the yield of extraction for three different steam flow rates (4, 7 and 9 L/min) and a packed bed of 100 g.

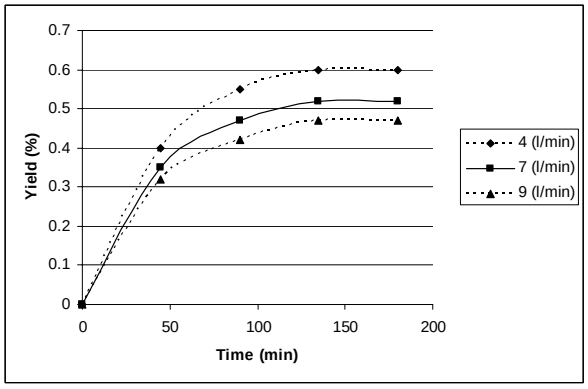

Figure 2. Yield curves of valerian oil samples for different steam flow rates.

It can be seen from Fig. 2 that as steam flow rate decreases, the amount of oil increases monotonically in each of the four time intervals. The highest yield was obtained for the steam flow rate of 4 L/min which was 0.6. Also, from the sharpness of curve during the first passed 50 minutes, it is observed that the highest extraction rate occurs in this interval. In most cases, up to 95 percent of total oil is extracted during the 135 minutes interval.

The effect of packed bed height on the extraction yield of essential oil was investigated for steam flow rate of 4 L/min in packed beds with heights of 30, 47.5 and 65 cm. These heights were equal to 100, 150 and 200 g of plant, respectively. The results presented in Fig. 3. revealed that the yield was reduced with the mass of the packed bed. Using 200 g of plant leaves resulted in the lowest yield while extraction of valerian oil from 100 g of the plant led to the highest yield of the process. Depending on the bed height, total yield decreased about 40 to 60 percent.

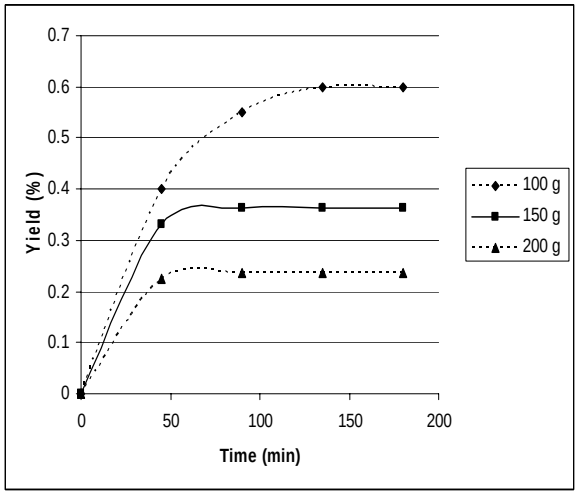

Figure 3. Yield curves of valerian oil samples for different masses of packed beds for steam flow rate of 4 L/min.

Furthermore, the slope of the curves for the packed beds of 47.5 and 65 cm of heights were less at the first passed 50 minutes in comparison with that of 35 cm height. The slope revealed that the amount of extraction was less in this interval for higher heights of column packed bed.

Increase in the height of the packed bed caused more pressure drop. As a result, steam passed the packed bed at higher speed.

Hence, the contact time between the steam and plant decreased dramatically and reduced the total yield of the extraction. To avoid this problem, steam redistributors were used along the column.

As can be seen in Fig. 4, using two or three beds caused an increase in the total yield of the extraction. The yield of such process in a one-bed column with a mass of 100 g and a steam flow rate of 4 L/min reached 0.6 percent compared to 0.65 percent reached in a three-stage column at the same conditions.

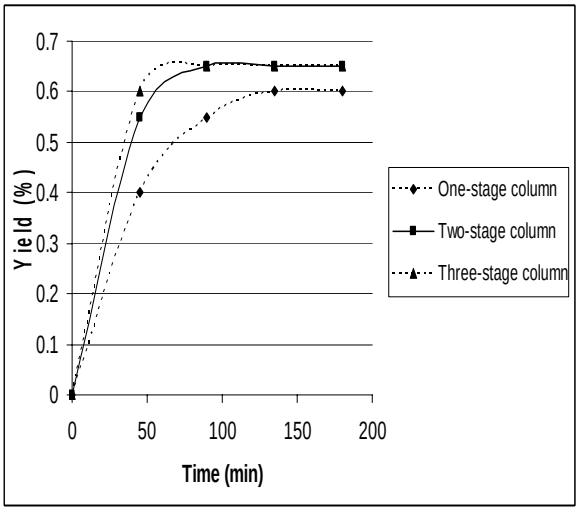

Figure 4. Yield curves of valerian oil samples in multistage column with steam flow rate of 4 L/min and packed bed of 100 g.

However, using more stages did not cause any increase in the total yield (data not shown).On the other hand, with a decrease in the height of the packed bed, a decrease in the steam channeling was observed. Here the contact between steam and the internal wall of the column increased which, in turn, caused the steam condensation on the internal wall of the distillation column.

Using multistage columns decreases the degree of steam channeling which is another reason for the yield increase. In this case, the effect of packed bed height on the pressure drop of each stage decreased, and steam had little tendency to move toward the walls.

The effects of crushing and distillation time on the oil yield are demonstrated in Figs. 5a and 5b for one and two-stage columns. The maximum yield obtained from the crushed root (particle size: 4mm) was significantly more than the maximum yield from the standard root (not crushed). These results were observed for two-stage columns. In these conditions the yield increased from 0.6 to approximately 0.7 percent.

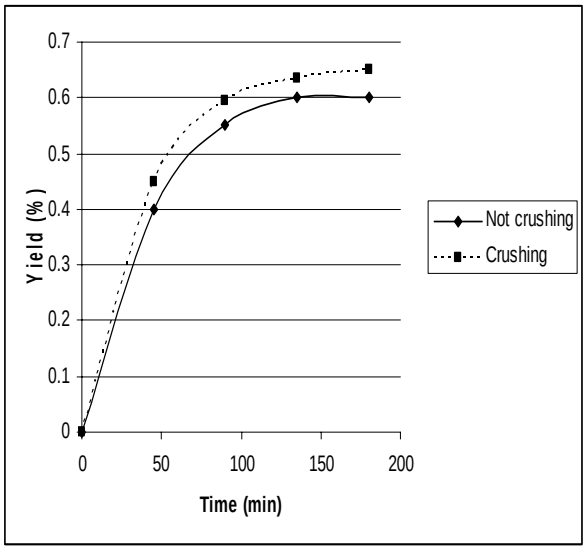

Figure 5a. Effect of plant crushing on yield of valerian oil in one stage column for 4 L/min steam flow rate and packed bed of 100 g.

For one stage distillation column, 95% of the maximum oil yield from the crushed roots after 136 minutes distillation was compared with 100 minutes for the standard roots. If distillation was stopped after 90 minutes, the oil yields from the crushed and standard roots were 0.6 and 0.55 %, respectively. Two stage distillation columns produced yields of

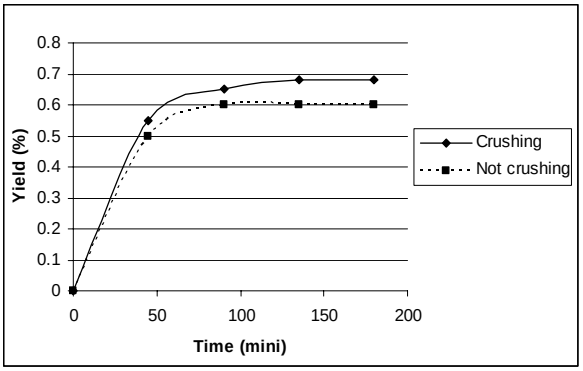

Figure 5b. Effect of crushing on yield of valerian oil in two stages column for 4 L/min steam flow rate and packed bed of 100 g.

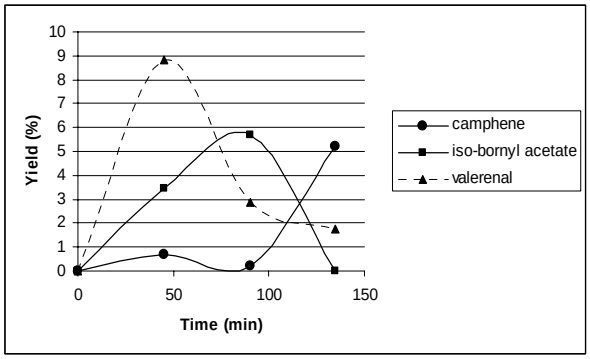

Figure 6. Yield of camphene, iso-bornyl acetate and valerenal in terms of time.

0.65 and 0.6% after 87 and 66 minutes respectively.

Table 1 lists the major monoterpenes found in this study. The results of GC-MASS analysis showed that valerian oil has 70 components with the concentration between 0.01 and 5.14 percent as compared to 47 components reported by [6] using hydrodistillation and CO_2 supercritical extraction techniques.

The results of gas chromatography were considered for one experiment with steam flow rate of 4 L/min and a packed bed with a mass of 100 g in two-stage column. Three of the most important components (camphene, iso-bornyl acetate and valerenal) were selected and changes of their concentration in relation to time of extraction were studied during 45, 90 and 135 min intervals (Fig. 6).

In Fig. 6 it was shown that a maximum extraction of isobornyl acetate and valerenal occurred after 45 and 90 minutes, respectively; after which both decreased with time.

For camphene, from 0-45 minutes the yield of extraction increased, followed by a minimum yield at 90 minutes. After 90 minutes, the yield sharply increased.

4. Discussion

The configuration of the system used in the present work is effective for extracting the essential oil of valerian. The results obtained in this work proves that extraction yield of valerian decreases with steam flow rate. Decrease in the steam flow rate increases the time of steam lingering in separation process. Consequently, the contact time between steam and plant tissue increases, which provides enough opportunity for essential oils to evaporate and be extracted.

A decrease in the steam flow rate improves the extraction process and, thus, economic aspects of work due to reduction in energy consumption.

Results of multistage column experiments confirms that an increase in the number of stages has a considerable effect on yield. However, this factor will subsides for the column with more than three stages, since by increasing the number of stages, steam contact with column walls increases and, consequently, steam condensation on walls occurs.

Table 1. Chemical composition (%) of the essential oils of *valerian*.

No.	KI.	Composite	%	No.	KI.	Composite	%
1	939	α-pinene	2.32	36	1494	Zingibenene	1.06
2	954	comphen	3.01	37	1495	Bicyclogermacene	2.66
3	975	Sabinene	0.12	38	1496	Valencene	0.44
4	979	β-pinene	0.91	39	1514	Δ-cadinene	0.52
5	984	3-octanone	0.28	40	1523	δ- cadinene	1.09
6	991	myrcene	0.29	41	1542	Kessane	2.30
7	1030	β-phylandrene	1.27	42	1547	valencene ketone	1.72
8	1031	1,8-cineole	0.74	43	1550	Elemole	1.19
9	1060	γ-terpinene	0.15	44	1569	Ledol	0.56
10	1089	terpinolene	0.11	45	1578	Spathulenol	1.18
11	1097	linalool	0.25	46	1583	caryophyllene oxide	1.20
12	1146	camphor	0.64	47	1584	neryl isovalerate	1.54
13	1169	borneol	0.54	48	1585	globulol	0.88
14	1177	linalool oxide	0.31	49	1593	viridifrolorol	0.41
15	1209	Nonbornene 2-methanol	0.53	50	1607	geranyl isovalerae	0.64
16	1245	carvacrol methyl ether	0.86	51	1646	T-muurolol	2.94
17	1289	isobornyl acetate	3.5	52	1651	β-eudesmol	0.99
18	1296	thujil acetate	0.49	53	1657	geranyl valerate	2.23
19	1300	n-tridecane	0.39	54	1658	valerian	1.10
20	1327	myrtenyl acetate	1.59	55	1662	kessyl alcohol	2.00
21	1338	Δ-elemene	3.11	56	1667	intermedeol	1.28
22	1349	α-terpinyl acetate	0.59	57	1671	valeranon	0.97
23	1371	cyclosativene	0.39	58	1675	(Z,E)-farneseol	0.75
24	1377	α-copaenen	0.18	59	1686	α-bisabolol	0.13
25	1390	iso-longifolene	0.30	60	1700	diepi α-cerdene	0.54
26	1391	β-elemene	1.09	61	1715	longifolol	0.60
27	1404	metyl eugenol	1.31	62	1717	valerenal	5.14
28	1410	α-gurjunene	1.30	63	1741	mintsulfide	0.24
29	1419	trans-caryophylene	2.77	64	1772	sesquiterpenoic acetate	0.33
30	1437	γ-elemene	1.51	65	1785	tranc-valerenyl acetatre	1.80
31	1440	α-guaiene	2.74	66	1806	kessyl acetate	1.68
32	1455	α-humulene	2.07	67	1826	cis-valerenyl acetate	1.26
33	1473	lynalyl-isovalerate	0.45	68	1856	kessanyl acetate	1.75
34	1483	γ-curcumene	0.46	69	1865	valerenic acetate	2.72
35	1485	d-germacene	2.03	70	1954	tranc-valerenyl isovalerate	1.32

An increase in height of the bed in the separation column causes a decrease in the process yield, because an increase in the height of the bed leads to an increase in pressure drop along the bed of plant which in turn, results in fast evaporation. Increasing the evaporation rate creates the phenomenon of channeling inside the bed. In other words, steam moves towards the walls and the contact surface between steam beds decreases.

Experiments showed variation in number of components with time. The results indicate a weak effect of time on the essential oil components. The time of distillation has an effect on the constituents of essential oil.

Effect of distillation time was studied for three important components of Valerian essential oil: camphene, iso-bornyl acetate and valerenal. Each of these components showed its own identity and different behavior during time intervals. Barrier effect and the boiling points of the components account for the differences. In the case of camphene, barrier effect is active and for isobornyl acetate and valerenal, the boiling point is effective. It should be noted that some of the camphene is present in the cell walls of the plant and some exists inside these cells. The yield increase and decrease are due to evaporation of compounds that exist between these cells. Another reason is the time required to destroy the cell walls that contains essential oils. But in the case of isobornyl acetate and valerenal, this trend is the result of their boiling points. 1,8-cineole has the boiling point of 176°C, and camphor has the boiling point of 209°C. As expected, the amount of 1,8-cineole, with a lower boiling point, decreases as time increases. It will take the first 15 minutes to see camphor evaporation; however, after this time, the amount of 1,8-cineole decreases as the time continues.

5. Conclusions

It was found that steam distillation in a multistage column is an effective extraction method for obtaining the essential oil of the valerian plant cultivated in Iran. Also, the maximum oil extraction occurred at low flow rates when the steam had long residence time in the packed bed because the steam had enough time to destroy the tissues of the plant. This study identified some important components of the valerian oil during steam distillation. In addition, the results showed that the duration of extraction should be at least 135 minutes, because more than 95% of the oil is extracted at the end of this time. By using steam distillation in this work, 70 components of essential oil of *Valeriana officinialis L.* Cultivated in Iran have been identified compared to 47 components reported by Safaralie *et al.* [6] using hydrodistillation and CO_2 supercritical extraction techniques.

Acknowledgment

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References

[1] Boutekedjiret, C., Bentahar, F., Belabbes R. and Bessiere, J., "Extraction of rosemary essential oil by steam distillation and hydrodistillation", Flavour and Fragrance J., 18, 481, (2003).

[2] Chemat, F., Lucchesi, M., Smadja, J., Favretto, L., Colnaghi, G. and Visinoni, F., "Microwave accelerated steam distil-lation of essential oil from lavender: A rapid and environmentally friendly approach", Analytica. Chimica Acta., 555, 157, (2002).

[3] Letchamo, W., Ward, W., Heard, B. and Heard, D., "Essential oil of valeriana officinalis L. cultivars and their antimicrobial activity as influenced by harvesting time under commercial organic cultivation", J. Agric. Food Chem., 52 (12), 3915, (2004).

[4] Masango, P., "Cleaner production of essential oils by steam distillation", J. Cleaner Production., 13, 833, (2005).

[5] Safaralie, A., Fatemi, Sh. and Salimi, A., "Experimental design on supercritical extraction of essential oil from valerian roots and study of optimal conditions", Food and Bioproducts Processing, 88, 312, (2010).

[6] Safaralie, A., Fatemi, Sh. and Sefidkon, F., "Essential oil composition of valeriana officinalis L. roots cultivated in Iran: Comparative analysis between supercritical CO_2 extraction and hydrodistillation", Journal of Chromatography A., 1180, 159, (2008).

[7] Smallfield, B.M., Van Klink, J.W., Perry, N.B. and Dodds, K.G., "Coriander spice oil: Effect of fruit crushing and distillation time on yield and composition", J. Agric. Food Chem., 49, 118, (2001).

[8] Tannous, P., Julini, R., Wang, M. and Simon, M., "Water balance in hydrosol production via steam distillation case study using Lavandin", J. Bioresource Technology, 84, 243, (2006).